LARGE FIRST HYPERPOLARIZABILITIES IN PUSH-PULL POLYENES BY TUNING BOND LENGTH ALTERNATION AND AROMATICITY

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Conjugated organic compounds with 3-phenyl-5-isoxazolone, or N, N'-diethylthiobarbituric acid acceptors have large first molecular hyperpolarizabilities (β) in comparison to compounds with 4-nitrophenyl acceptors as measured by electric field induced second harmonic generation, (EFISH), in chloroform, with 1.907 μm fundamental radiation. For example, julolidinyl-$(CH=CH)_3$ -CH= N, N'-diethylthiobarbituric acid, 2[3], that has 12 atoms between the nitrogen donor atom and acceptor carbonyl group has a $\beta(0)$ of 911 x 10^{-30} esu (after correcting for dispersion with a two-state model), whereas $(CH_3)_2NC_6H_4-(CH=CH)_4-C_6H_4NO_2$, 5[4], that has 16 atoms, between its donor and acceptor has a $\beta(0)$ of 133 x 10^{-30} esu.

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Using a two-state model,(*1*, 2, 3) it was shown that there is an optimal combination of donor and acceptor strengths for a given bridge that will lead to the correct balance of electron asymmetry and polarizability to maximize the first hyperpolarizability β. (4) We have now been exploring the hypothesis that the difference between the average lengths of carbon-carbon single and double bonds in donor-acceptor substituted polyene and polymethine dyes, i.e. their bond length alternation (<Δr>) is a useful structural parameter to examine when establishing generalized structure-property relationships for organic materials exhibiting second-order nonlinear optical (NLO) effects. (5, *6*) Reduction of bond length alternation takes a molecule from the bond-alternate polyene limit (in which only one canonical resonance structure contributes predominantly to the ground state of the molecule) to the bond-equivalent cyanine limit (in which two canonical resonance structures contribute equally to the ground-state structure of the molecule). (7, 8, 9) Electric field dependent calculations of molecular geometry and β indicate that for highly bond length alternated molecules, such as polyenes with weak donors and acceptors, β is positive, then as a function of increasing polarization and decreasing <Δr>, β first increases, peaks in a positive sense, decreases, crosses through zero at the cyanine-limit where <Δr> = O Å, (Fig. 1) and then becomes negative when the ground state of the molecule is zwitterionic. (*5, 6*) From these calculations we estimated that the positive peak for β occurs at roughly <Δr> = 0.03 to 0.05Å.(*5, 6*) Most molecules that have been examined in the past, such as donor-acceptor substituted stilbenes(*10*) or diphenyl polyenes), do not have sufficiently strong donors and acceptors to give the correct <Δr> needed to maximize β. The high degree of bond length alternation observed in the central polyene bridge of donor-acceptor substituted stilbenes and related molecules is indicative of an insufficient contribution of the charge-separated resonance form to the ground-state configuration of the molecules and is a consequence of the loss of aromatic stabilization in the charge-separated form. We therefore designed donor-acceptor polyenes where the loss of aromaticity in one end upon charge-separation (in the case the donor end) would be somewhat offset by a gain in arornaticity upon charge-separation in the opposite end. We predicted that such molecules would have more nearly the correct contribution of the charge-separated form to the ground-state structure required to reach the bond length alternation at which β is maximized.

We report that compounds with acceptors that can gain aromaticity in their charge-separated resonance forms, such as $(CH_3)_2NC_6H_4$-$(CH=CH)_n$-A and julolidinyl-

$(CH=CH)_n$- A, where A is, N, N'-diethylthiobarbituric acid, (series 1 **[n]** or 2 **[n]** respectively) or 3-phenyl-5-isoxazolone (series **3[n]** or **4[n]** respectively) for n = O-3 (Fig. 2), have large β values and reduced $<\Delta r>$ in comparison with compounds where A = $C_6H_4NO_2$. If stable polymers incorporating molecules with these large hyperpolarizabilities can be fabricated, a variety of through-plane thin film electrooptic devices, such as spatial light modulators, could be realized.

We synthesized the molecules in Fig. 2 by reaction of 3-phenyl-5-isoxazolone or N, N'-diethylthiobarbituric acid with (N,N-dimethylamino)pheny l-($CH=CH)_nCHO$, julolindinyl-$(CH=CH)_nCHO$ or (where n is as defined in Fig. 2) julolidinyl-$(CH=CH)_2$-$C(CH_3)=CH-CH=CH-CH=C(CH_3)$-$CH=CH$-$CHO$(*11*) under standard Knoevenagel conditions. We characterized the compounds by 'H nuclear magnetic resonance and ultraviolet visible spectroscopy as well as elemental analysis and/or mass spectroscopy. We expected that the potential gain in aromaticity upon charge separation (Fig. 3) would lead to a substantial charge transfer and reduced bond length alternation in the ground state. Thus, molecules containing acceptors whose topology dictates that aromaticity is gained upon charge separation (such as 3-phenyl-5-isoxazolone or N, N'-diethyl-thiobarbituric acid) would have more nearly the correct degree of bond length alternation needed to optimize β and could thus give rise to extremely large optical nonlinearities compared to conventional molecules of similar length.

We measured the hyperpolarizabilities by electric field induced second harmonic generation (EFISH) (*13*, 14, *15,16*) in chloroform, with 1.907 μm fundamental radiation. The values of β we obtained support the hypothesis that molecules of only moderate lengths containing the 3-phenyl-5-isoxazolone or N, N'-diethyl-thiobarbituric acid acceptor can have unprecedented β values (Table 1). The dispersion-corrected (*1*, 2, 3) $\beta(0)$ and $\mu\beta(0)$ values of the n = O and 1 compounds, which are analogous to ones previously reported,(*17,18,19*) are not exceptional in comparison to other molecules in the literature. However, the longer n = 2 and 3 vinylogs exhibit strikingly large $\beta(0)$ and $\mu\beta(0)$ values, (Table 1) for their lengths. The importance of the topology of the π system is clearly illustrated if one considers that both $(CH_3)_2NC_6H_4$-$CH=CH$-C_6H_4CHO, **6,** and julolidinyl-$(CH=CH)_2$-$CH= N$, N'-diethylthiobarbituric acid, 2[2], ten conjugated atoms between the amine donor to the carbonyl acceptor, yet the former has a $\beta(0)$ of 20 x 10^{-30} esu, whereas the latter compound has $\beta(0)$ of 490 x 10^{-30} esu. To our knowledge, no compounds with values of $\mu\beta$ greater than 10,000 x 10-48 esu have been reported and thus, the β and $\mu\beta$ values for the longer compounds in the table are without precedent. In

particular, the dispersion-corrected $\mu\beta(0)$ julolidinyl-$(CH=CH)_2$-C(CH3)=CH-CH=CH-CH=C(CH3-CH=CH-CH= N, N'-diethyl-thiobarbituric acid, 2'[6] ~15,000x 10^{-48} esu is more than 40 times that of $(CH_3)_2NC_6H_4$-CH=CH-$C_6H_4NO_2$, 5[1], $\mu\beta(0) = 363$ x 10^{-48} esu, which is commonly used in poled polymer applications. This exceptionally high value is not surprising since it has been demonstrated that donor-acceptor substituted carotenoids can display large quadratic nonlinearities.(20, *21*) Preliminary experiments indicate that poled polymers containing **1** [3] exhibit a large electrooptic coefficient (r_{33}). (22)

We performed single crystal X-ray determinations on julolidinyl-$(CH=CH)_2$-CH= 3-phenyl-5-isoxazolone, 4[2], and julolidinyl-$(CH=CH)_3$-CH= 3-phenyl-5-isoxazolone, 4[3],(23) to provide experimental evidence for the decrease in bond length alternation in these highly nonlinear compounds.   Their molecular structure as determined from the crystallographic analysis along with selected bond lengths are shown in Fig. 4. Several points about the structures are worth noting. First, the julolidinyl rings exhibit significant quinoidal character, as evidenced by the unequal carbon-carbon bond lengths in the rings (Fig. 4). Second, the difference in length between adjacent carbon-carbon bonds increases upon going from the acceptor (3-phenyl-5-isoxazolone) end to the donor (julolidinyl) end of the molecule. Perhaps this can be viewed as a result of the acceptor 'pulling' on the π electrons more than the donor is 'pushing' on them. Whatever the case, the observation that bond length alternation is not constant across the length of the polymethine chain is general to eight donor-acceptor polyene compounds we have crystallographically characterized and may ultimately limit the utility of using a single parameter, <Δr>, to describe the degree of ground-state polarization in a molecule. Third, 4[2], and 4[3], have <Δr> = 0,05 and 0.03 Å respectively. For comparison, <Δr> in simple polyenes is 0.11 Å, from the crystal structure of 1,3,5,7-octatetraene(24) and diphenyl- 1,3,5,7-octatetraene(25) and <Δr> for the non-ring carbon-carbon bonds in a donor-acceptor substituted stilbene is 0.14 Å from the crystal structure of 2-methoxy-4'-nitro stilbene.(*10*). Thus, the values for the 3-phenyl-5-isoxazolone acceptor substituted compounds are significantly lower than that found in the polyene and stilbene compounds mentioned above and are close to the values we predict are needed to optimize β. However, as noted earlier, (26) care must be taken when using solid-state structural data to gain insight about molecular structure in solution. In general, we have found that the solid state behaves like an especially polar environment, which tends to result a relatively high degree of charge separation and in this case a somewhat low <Δr> relative to that which might be found for the molecule in a moderately polar solvent such as chloroform.

Based upon previously studies, we estimate that the difference between $<\Delta r>$ in the solid state and in chloroform is less than -0.03 Å and thus the structural data reported here provide strong evidence for reduced $<\Delta r>$ in 3-phenyl-5-isoxazolone substituted compounds.

In conclusion, we have demonstrated 3-phenyl-5-isoxazolone and N, N'-diethylthiobarbituric acid-containing derivatives can exhibit very large nonlinearities in comparison to compounds with nitro or simple carbon yl acceptors, but with bridges that are strongly aromatic. Thus, the greater than twenty-five fold enhancement of $\beta(0)$ for 2[2] as compared to 6 illustrates that judicious manipulation of the π electron system is the key to optimizing hyperpolarizability. The crystallographic structural data provided here demonstrates that molecules that have acceptors that can gain aromaticity upon charge separation have $<\Delta r>$ significantly lower than those values found in polyenes or stilbenes where $<\Delta r>$ is greater than 0.12 Å. Thus, our strategy of reducing bond length alternation by tuning the relative contributions of neutral and charge-separated resonance to the ground-state structure has led to molecules with unprecedented nonlinearities and may result in promising new materials for electrooptic modulator applications. (27)

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23. for 4[2]: $C_{26}H_{24}N_2O_2$, M. wt. 396.49. Monoclinic, $P2_1/n$ (#14), $\underline{a} = 9.372(3)$Å, $\underline{b} = 21.457(7)$Å, $\underline{c} = 10.828(3)$Å, $\beta = 11\ 1.67(2)0$, $V = 2023.6(12)$Å^3, $Z = 4$. (figures in parentheses are the estimated standard deviations in the last figure). MoKα radiation, 4267 reflns. collected, 1879 independent used in refinement, full matrix

least squares, R ($= \Sigma |F_o - |F_c||/ \Sigma F_o$, where F_o and F_c are the observed and the calculated structure factors) for 1632 reflns. with F. $> 0 = 0,092$, goodness of fit ($[\Sigma\, w\, (F_0^2 - F_c^2)^2 / (n - p)]^{1/2}$, where w = the weight of the reflection, n = the number of data, and p = the number of parameters refined)= 1.16. All non-hydrogens refined anisotropically. Hydrogen atom parameters assigned from difference maps or by calculation with C-H= 0.95Å. for **4[3]**: $C_{28}H_{26}N_2O_2$, M. wt. 422.53. Monoclinic, P2$_1$/n (#14), $\underline{a}$ = 9.551 (2)Å, $\underline{b}$ = 22.787 (6)Å, $\underline{c}$ = 10.688 (2)Å, β = 109.61(2)0, V = 2191 .2(9)Å^3, Z = 4. (Figures in parentheses are as defined above). MoKα radiation, 7047 reflns. collected, 2669 independent used in refinement, full matrix least squares, R (as above) for 1632 reflns. with F. $> 0 = 0,065$, goodness of fit (as above)= 1.41. All non-hydrogens refined anisotropically. Hydrogen atom parameters placed by calculation with C-H = 0.95Å and repositioned once before final least squares cycle.

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TABLE

Table 1. Selected linear and nonlinear optical data for compounds of the form in Fig. 1

Cmpd #	λ_{max} (rim)	μ /10^{-18} (esu)[a]	β /10^{-30} (esu)[a]	$\beta(0)$/10^{-30} (esu)[a]	$\mu\beta$/10^{-48} (esu)[a]	$\mu\beta(0)$/10^{-48} (esu)[a]
1 [0][b]	484	5.4	68	48	370	259
1[1][b]	572	5.7	256	150	1457	855
1[2]	604	6.2	636	347	3945	2151
1[3]	624	6.6	1490	772	9831	5095
2[0]	522	7.0	87	56	609	394
2[1]	614	6.6	355	186	2210	1159
2[2]	680	6.3	1141	490	7152	3069
2[3]	686	8.8	2169	911	19086	8019
2'[6]	680				34770	14920
3[0]	478	8.3	37	27	312	221
3[1]	530	8.6	90	186	1202	771
3[2]	562	8.7	362	218	3156	1895
3[3]	582	8.9	528	300	8171	4696
4[0]	504	9.5	51	34	488	328
4[1]	586	9.1	101	180	1638	919
4[2]	620	9.0	656	339	5812	3000
4[3]	640	9.8	995	485	9750	4753
4'[6]	647	16	1781	849	28500	13600
5[1]	430	6.6	73	55	482	363
5[2]	442	7.6	107	80	813	608
5[3]	458	8.2	131	95	1074	779
5[4]	464	9	190	133	1700	1197
6	360	3.5	24	20	84	70

a: The error in the measurements is estimated to be ±20%. The β values have not been corrected for the electronic deformation contribution to the EFISH signal.

b: $\mu\beta$ values of the N, N'-dimethylthiobarbituric acid analogs of the n = O and 1 compounds, measured at 1.34 and 1.064 μm have been reported previous] y.(17-19)
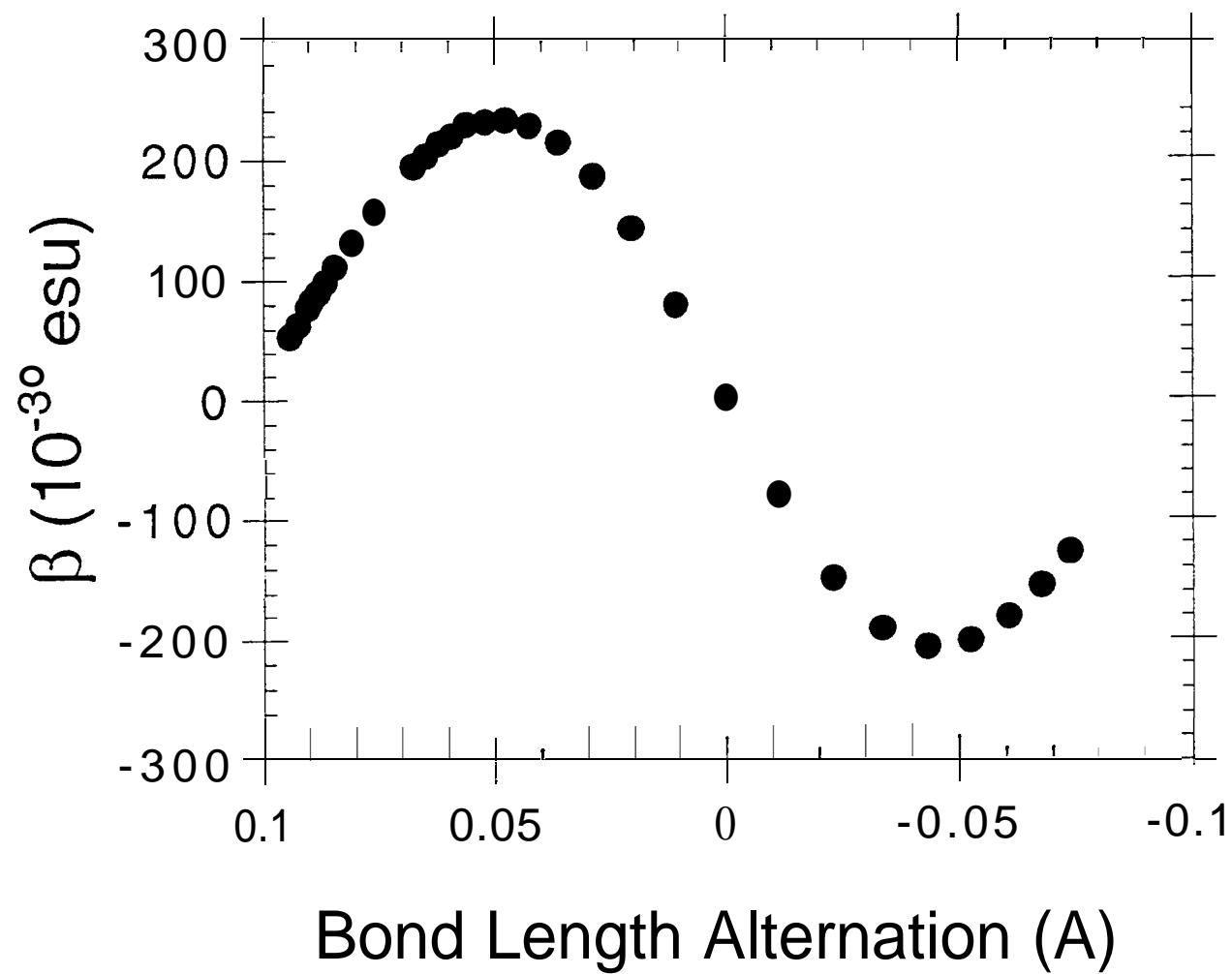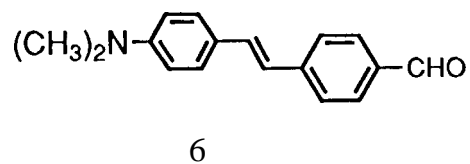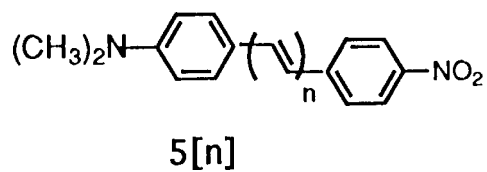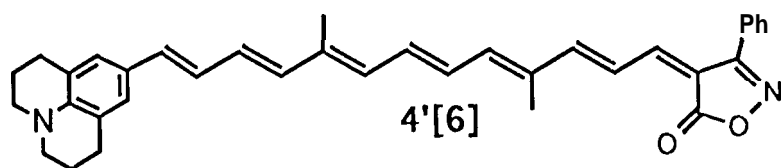
FIGURE CAPTIONS

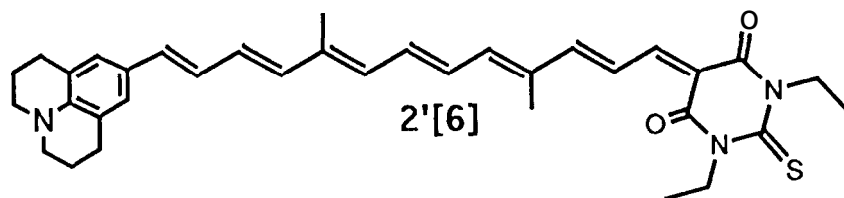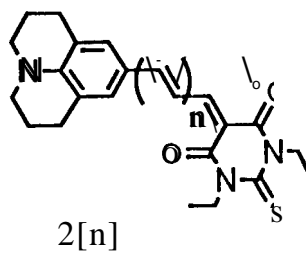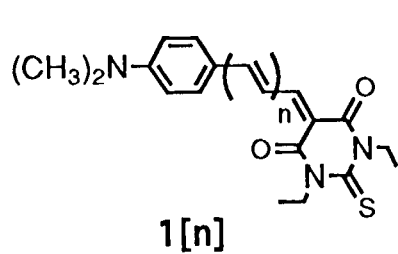**Fig. 1,** Plot of β versus $<\Delta r>$, generated using an AM 1 geometry optimization (in the MOPAC package) for $(CH_3)_2N\text{-}(CH=CH)_4\text{-}CHO$ in the presence of a static electric-field (generated using point-charges) of varying strength (5,6). For each value of the static field, and thus $<\Delta r>$, β was calculated using a finite field procedure.

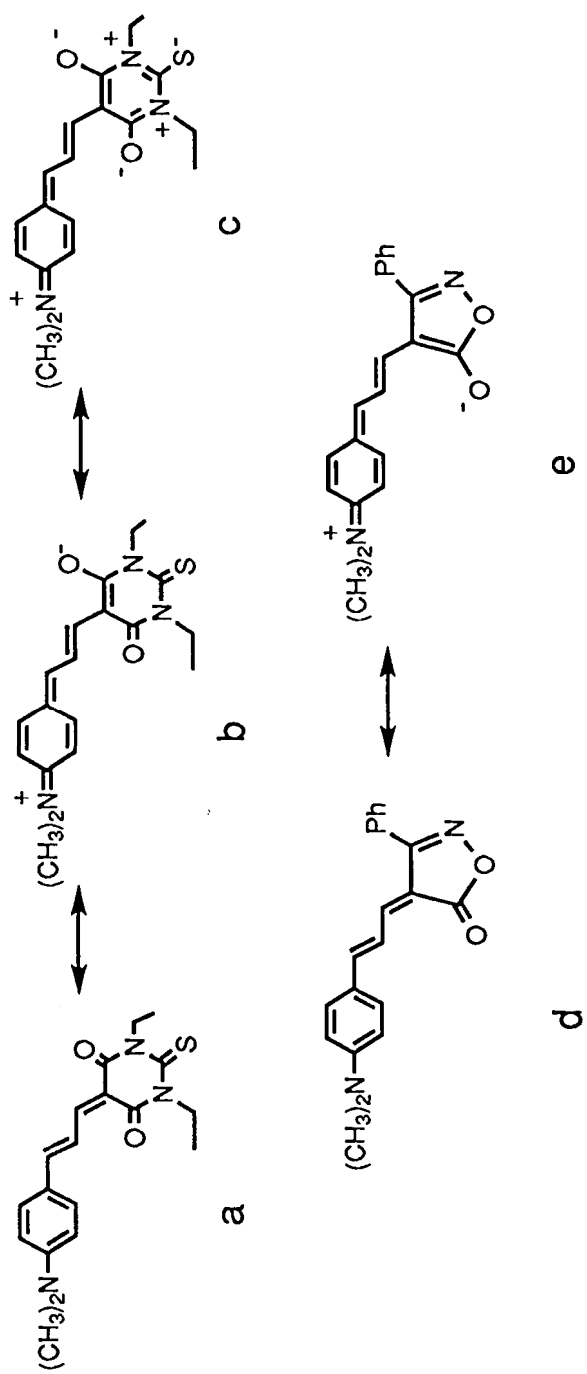**Fig.** 2. Structure and labelling scheme for compounds investigated in this study.

Fig. 3. For compound 1[1] a: neutral resonance form, b: one of the charge separated resonance forms, and c: a charge separated resonance form in which the acceptor ring has aromatic character. For compound 3[1] d: neutral resonance form and e: a charge separated resonance form in which the acceptor ring has aromatic character.

Fig. 4. ORTEP drawings of the molecules with 50% probability ellipsoids showing the bond lengths for the conjugated pathway between then donor and the acceptor for A: 4[2] and B: 4[3]. Hydrogen atoms in both structures are shown with thermal parameters one-tength those assigned.

β (10^{-30} esu) vs Bond Length Alternation (A)

Fig 1

where n = 0,1,2,3

Fig 3

A

1.367(8)
1.420(8)
1.403(8)
1.434(8)
1.358(7)
1.357(8)
1.397(8)
1.374(8)
1.401(8)
1.391(8)

B

1.371(4)
1.413(4)
1.399(4)
1.429(4)
1.366(4)
1.350(4)
1.408(4)
1.357(4)
1.404(4)
1.364(4)
1.399(4)
1.372(4)
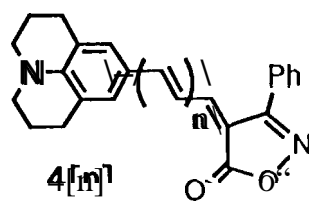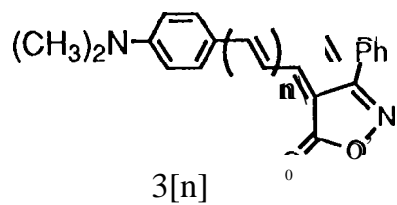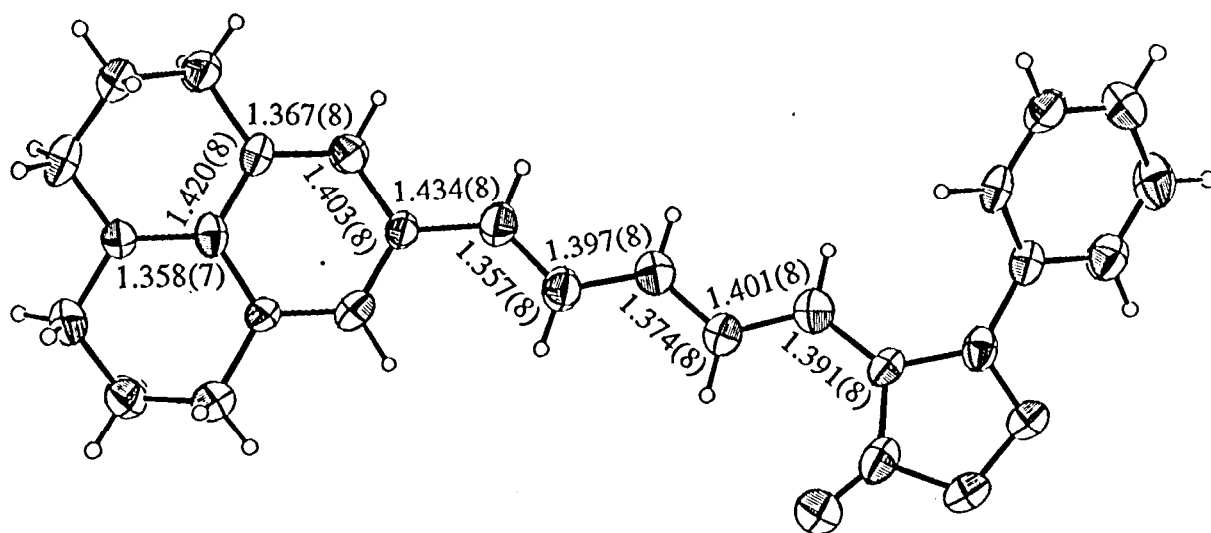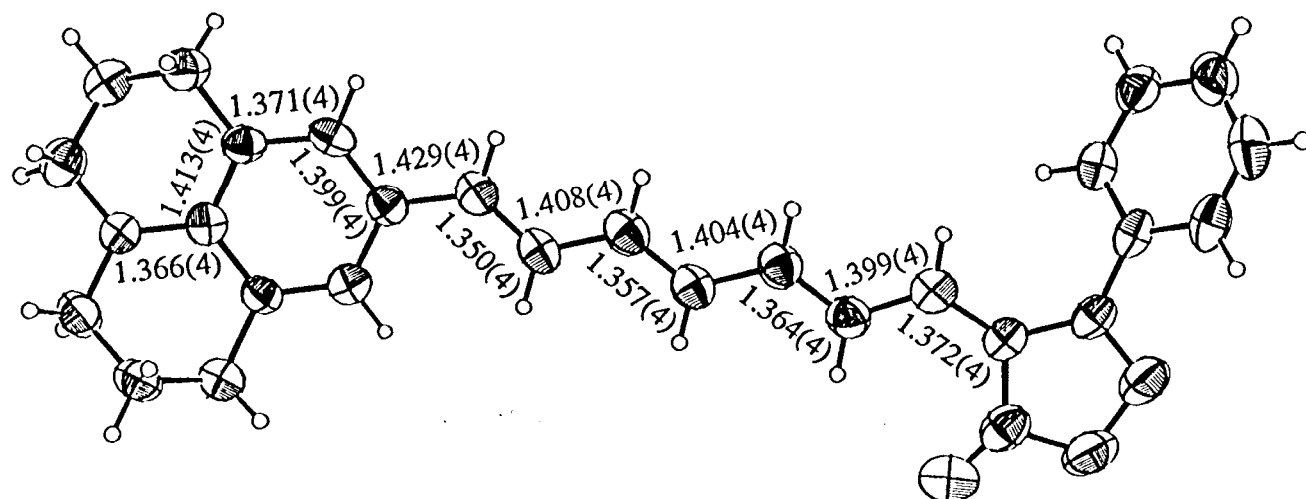
Characterizing data for compounds investigated in this study

Unless indicated, NMR spectra were recorded in $CDCl_3$.

1[0]: ^{1}H NMR δ 8.40 (din, J = 9.2 Hz, 2H), 8.39 (s, lH), 6.68 (din, J = 9.3 Hz, 2H), **4.56,4.55** (each q, J = 7.0 Hz, 2H), 3.15 (s, 6H), 1.30, 1.28 (each t, J = 7.0 Hz, 3H). ^{13}C NMR δ 178.80, 162.21, 159.79, 159.39, 154.75, 139.95, 121.59, 111,16, 110.27, 43.96,43.41,40.14, 12.49, 12.43. Anal. Calcd. for $C_{17}H_{21}N_3O_2S$: C, 61.61; H, 6.39; N, 12.68. Found: C, 61.70; H, 6.43; N, 12.71. λ_{max} (solvent, nanometers): cyclohexane, 468; toluene, 484; chloroform, 494; methylene chloride, 494; acetone, 492; methanol, 494; N-methyl-2-pyrrolidone, 504.

1[1]: ^{1}H NMR δ (CD_2Cl_2) 8.45 (old, J = 14.8, 12.6 Hz, lH), 8.17 (d, J = 12.4 Hz, 1H), 7.62 (d, J = 8.9 Hz, 2H), 7.48 (d, J = 14.8 Hz, 1H), 6.71 (d, J = 9.0 Hz, 2H), 4.54, 4.52 (each q, J = 7.1 Hz, 2H), 3.11 (s, 6H), 1.28, 1.26 (each t, J = 6.9 Hz, 3H). ^{13}C NMR δ 178.80, 161.13, 160.22, 159.67, 158.35, 153.31, 132.66, 123.49, 121.09, 111.87, 110.46,43.51,42.97,40.14, 12.47, 12.42; Anal. Calcd. for $C_{19}H_{23}N_3O_2S$: C, 63.84; H, 6.49; N, 11.75. Found: C, 63.88; H, 6.52; N, 11.71. λ_{max} (solvent, nanometers): cyclohexane, 530; toluene, 550; chloroform, 572; methylene chloride, 570; acetone, 564; methanol, 574; N-methyl-2-pyrrolidone, 582.

1[2]: ^{1}H NMR δ (CD_2Cl_2) 8.06 (m, 2H), 7.45 (d, J = 8.9 Hz, 2H), 7.37 (old, J = 13.8, J = 11.0 Hz, 1H), 7.05 (m, 2H), 6.69 (d, J = 8.9 Hz, 2H), 4.51 (m, 4H), 3.06 (s, 6H),

1,27 (m, 6H). ^{13}C NMR δ]78,80,]60.97, 159,93, 158.43, 158.32, 151.98, 147.09, 130.33, 127.42, 123.94, 123.82, 112.00, 111.57,43.53,43.01,40.09, 12.44, 12.42; Anal. Calcd. for $C_{21}H_{25}N_3O_2S$: C, 65.77; H, 6.57; N, 10.96. Found: C, 65.86; H, 6.57; N, 10.97. λ_{max} (solvent, nanometers): cyclohexane, 544; toluene, 570; chloroform, 604; methylene chloride, 600; acetone, 586; methanol, 598; N-methyl-2-pyrrolidone, 633.

1[3]: ^1H NMR δ 8.09 (d, J = 12.6 Hz, lH), 8.00 (apparent t, J = 13.3 Hz, 1H), 7.39 (d, J = 9.0 Hz, 2H), 7,25 (old, J = 14.0, 11.7 Hz,1H), 6.96 (old, J = 14.4, 10.2 Hz, 1H), 6.85 (d, J = 15.1 Hz, 1H), 6.81 (old, J = 15.1, 10.2 Hz, lH), 6.67 (d, J = 9.0 Hz, 2H), 6.59 (old, J = 14.3, 11.7 Hz, lH), 4.55,4.54 (each q, J = 7.0 Hz, 2H), 3.04 (s, 6H),1.30 (m, 6H). ^{13}C NMR 5178.75, 160.87, 159.87, 157.99, 157.27, 151.19, 147.82, 142.07, 130.07, 129.28, 128.31, 124.30, 123.92, 112.10, 112.00, 43.58, 43.05, 40.15, 12.42 (coincident). Anal. Calcd. for $C_{23}H_{27}N_3O_2S$: C, 67.45; H, 6.65; N, 10.26. Found: C, 67.48; H, 6.71; N, 10.18. λ_{max} (solvent, nanometers): cyclohexane, 556; toluene, 588; chloroform, 624; methylene chloride, 612; acetone, 592; methanol, 608; N-methyl-2-pyrrolidone, 634.

2[0]: ^1H NMR (CD_2Cl_2) δ 8.22 (s, lH), 8.08 (brs, 2H), 4.57, 4.54 (each q, J = 7.0 Hz, 2H), 3.40 (apparent t, J = 5.8 Hz, 4H), 2.77 (apparent t, J = 6.2 Hz, 4H), 1.98 (m, 4H), 1.29, 1.26 (each t, J = 6.9 Hz, 3H). ^{13}C NMR 6178.60, 162.50, 159.47, 158.87, 149.92, 137.79, 121.15, 120.57, 108.17, 50.61,43.86,43.22,27.46, 20.96, 12.54, 12.44. Anal. Calcd. for $C_{21}H_{25}N_3O_2S$: C, 65.77; H, 6.57; N, 10.96; S, 8.36. Found: C, 65.82; H, 6.65; N, 10.97; S, 8.40. λ_{max} (solvent, nanometers): cyclohexane, 492; chloroform, 522.

2[1]: ^1H NMR (CD_3COCD_3) δ 8.40 (old, J = 14.5, 12.7 Hz, 1H), 8.10 (old, J = 12.6, 0.5 Hz, 1H), 7.56 (d, J = 14.5 Hz, 1H), 7.27 (brs, 2H), 4.52,4.50 (each q, J = 6.9

Hz, 2H), 3.43 (apparent t, J = 5.8 Hz, 4H), 2.78 (apparent t, J = 6.5 Hz, 4H), 1,96 (m, 4H), 1.25, 1.22 (each t, J = 6.9 Hz, 3H). ^{13}C NMR δ 178.60, 161.37, 160.46, 159.38, 159,18, 147.99, 130.78, 122.74, 121.46, 120.11, 108.46, 50.33, 43.41, 42.86, 27.40, 21.04, 12.49, 12.41. Anal. Calcd. for C23H27N302S: C, 67.45; H, 6.65; N, 10.26; S, 7.83. Found: C, 67.18; H, 6.67; N, 10.24; S, 7.77. λmax (solvent, nanometers): cyclohexane, 563; chloroform, 614 (loge, 5.08).

2[2]: ^{1}H NMR δ (CD2Cl2) 8.07 (d, J = 12.8 Hz, lH), 7.98 (apparent t, J = 13.2 Hz, 1H), 7.37 (old, J = 14, 11.0 Hz, 1H), 7.03 (brs, 2H), 6.98 (m, 2H), 4.54 (m, 4H), 3.30 (apparent t, J = 5.8 Hz, 4H), 2.73 (apparent t, J = 6.3 Hz, 4H), 1.95 (m, 4H), 1.27, 1,25 (each t, J = 7.0 Hz, 3H). Anal. Calcd. for C25H29N302S: C, 68.94; H, 6.71; N, 9.65; S, 7.36. Found: C, 69.03; H, 6.76; N, 9.63; S, 7.42. λmax (solvent, nanometers): cyclohexane, 580; chloroform, 684.

2[3]: ^{1}H NMR δ 8.08 (d, J = 12.7 Hz, 1H), 7.98 (apparent t, J = 13.3 Hz, 1H), 7.25 (old, J = 13.8, J = 11.9 Hz, 1H), 6.96, (bs, 2H), 6.95 (m, 1H), 6.55 (old, J = 14.1, J = 11.8 Hz, 1H), 4.55,4.54 (each q, J = 6.9 Hz, 2H), 3.25 (apparent t, J = 5.7 Hz, 4H), 2.74 (apparent t, J = 6.3 Hz, 4H), 1.96 (m, 4H), 1.31, 1.29 (each t, J = 7.3 Hz, 3H). ^{13}C NMR 5178.05, 161.05, 160.04, 157.97, 157.91, 148.80, 144.72, 143.22, 129.39, 127.81, 127.30, 123.39, 123.09, 121.28, 111.35,50.02,43.58,43.04, 27.67,21.53, 12.48, 12.44; ElMS, m/z 461(M, 2), 327(47), 199(54), 186(100), 170(32), 97(24), 69(34); EI HRMS m/z (calcd for C27H31N3O2S: 461 .2150),461 .2137. Anal. Calcd. for C27H31N3O2S: C, 70.25; H, 6.77; N, 9. 10; S, 6.95. Found: C, 70.03; H, 6.80; N, 9.00; S, 6.83. λmax (solvent, nanometers): chloroform, 686, (log ε 4.82).

2'[6]: ^{1}H NMR (CD2Cl2) 87.95-8.2 (m:ABX, 2H), 7.15-7.35 (m:ABX, 1H), 7.03 (apparent t, J = 12.5 Hz, 1H), 6.86 (bs, 2H), 6.2-6.8 (m, 7H), 4.52,4.51 (each q, J =

6.8 Hz, 2H), 3.18 (t, J = 5.6 Hz, 4H), 2.72 (t, J = 6.2 Hz, 4H), 2.08 (s, 3H), 2.04, (s, 3H), 1.87-2.0 (m, max at 1.94, 4H), 1.27, 1.25 (each t, J = 6.9 Hz, 3H); DCIMS, M+1 = 468.

3[0]: ^{1}H NMR (CD$_2$Cl$_2$) δ 8.38 (br d, J = 8.6 Hz, 2H), 7.56 (m, 5H), 7.39 (s, 1H), 6.74 (d m, J = 9.3 Hz, 2H), 3.15 (s, 6H); ^{13}C NMR δ 170.38, 164.69, 154.39, 151.70, 137.96, 130.25, 128.93, 128.76, 128,55, 121.61, 111.43, 109.59, 40.17; Anal, Calcd. for C$_{18}$H$_{16}$N$_2$O$_2$: C, 73.96; H, 5.52; N, 9.58. Found: C, 74.08; H, 5.54; N, 9.57. λ_{max} (solvent, nanometers): cyclohexane, 441; toluene, 466; chloroform, 478; methylene chloride, 478; acetone, 474; methanol, 482; N-methyl-2-pyrrolidone, 486.

3[1]: ^{1}H NMR (CD$_2$Cl$_2$) δ 8.19 (old, J = 14.9, 12.1 Hz, 1H), 7.61 (m, 2H), 7.57 (din, J = 8.9 Hz, 2H), 7.55 (m, 3H), 7.47 (old, J = 12.0,0.5 Hz, lH), 7.27 (d, J = 14.9 Hz, 1H), 6.70 (din, J = 9.1 Hz, 2H), 3.08 (s, 6H); ^{13}C NMR 6170.66, 162,50, 154.59, 152.96, 151.15, 131.99, 130.44, 129.01, 128.30, 12.8.19, 123.07, 118.34, 111.88, 110.94, 40.09; Anal. Calcd. forC20H18N2C)2 : C, 75.45; H, 5.70; N, 8.80. Found: C, 75.39; H, 5.69; N, 8.74. λ_{max} (solvent, nanometers): cyclohexane, 486; toluene, 508; chloroform, 530; methylene chloride, 534; acetone, 526; methanol, 548; N-methyl-2-pyrrolidone, 550.

3[2]: ^{1}H NMR δ (CD$_2$Cl$_2$) 7.81 (old, J = 14.1, 12.3 Hz, 1H), 7.57 (m, 5H, Hal), 7.43 (d m, J = 9.0 Hz, 2H), 7.40 (old, J = 12.6,0.5 Hz, 1H), 7.18 (apparent dddd, J = 14.3, 7.4,3 .3,0.4 Hz, 1H), 7.00 (m, 2H), 6.69 (d m, J = 9.0 Hz, 2H, He), 3.04 (s, 6H, Ha); ^{13}C NMR (125.8 MHz) 8170.21, 162.40, 154.61, 151.92, 149.73, 145,57, 130.53, 130.02, 129.06, 128.31, 128.24, 124.72, 123,93, 123.72, 112.70, 112.09, 40.08; Anal. Calcd. for C$_{22}$H$_{20}$N$_2$O$_2$: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.67; H, 5.90; N, 8.08. λ_{max} (solvent, nanometers): cyclohexane, 508; toluene, 538; chloroform, 562; methylene chloride, 564; acetone, 553; methanol, 570; N-methyl-2-pyrrolidone, 580.

3[3]: ^{1}H NMR (CD$_2$Cl$_2$) δ 7.78 (old, J = 14.3, 12,3 Hz, 1H, Hf), 7.58 (m, 5H), 7.37 (m, 3H), 7.09 (old, J = 14.4, 11.6 Hz, 1H), 6.90 (apparent ddd, J = 14.1,7 .0,3.8 Hz), 6.82 (m, 2H), 6.67 (d m, J = 9.0 Hz, 2H), 6.62 (old, J = 13.6, 11.6 Hz, 1H), 3.01 (s, 6H); ^{13}C NMR (125.8 MHz) δ 170.01, 162.37, 153.50, 151.22, 149.35, 146.27, 141.14, 130.59, 129.81, 129.09, 129.07, 128.22, 128.17, 125.64, 124.48, 123,97, 113.40, 112.12, 40.15. Anal. Calcd. for C24H22N202: C, 77.81; H, 5.99; N, 7.56, Found: C, 77.89; H, 6.02; N, 7.53. λ_{max} (solvent, nanometers): cyclohexane, 534; toluene, 558; chloroform, 582; methylene chloride, 578; acetone, 566; methanol, 576; N-methyl-2-pyrrolidone, 592

4[0]: ^{1}H NMR (CD$_3$COCD$_3$) δ 8.08 (v br s, 2H), 7.58 (m, 5H), 7.31 (s, lH), 3.46 (apparent t, J = 5.8 Hz, 4H), 2.73 (apparent t, J = 6.2 Hz, 4H), 1,95 (m, 4H). ^{13}C NMR 5164.85, 150.89, 149.27, 135.55, 135.49, 129.96, 128.97, 128.79, 128.73, 121.05, 120.85, 107.03,50,43,27.32, 20.82; Anal. Calcd. for C22H20N2O2: C, 76.72; H, 5.85; N, 8.13. Found: C, 76.82; H, 5.87; N, 8.09, λ_{max} (solvent, nanometers): cyclohexane, 476; chloroform, 504.

4[1]: ^{1}H NMR (CD$_3$COCD$_3$) δ 8.12 (dd J = 14.7, 12.2Hz, 1H), 7.66 (m, 2H), 7.61 (old, J = 12.2,0.6 Hz, lH), 7.56 (m, 3H), 7.42 (d, J = 14.6 Hz, 1H), 7.17 (s, 2H), 3.38 (apparent t, J = 5.8 Hz, 4H), 2.75 (apparent t, J = 6.2 Hz, 4H), 1.94 (m, 4H). ^{13}C NMR (125.8 MHz) 6171.10, 162.47, 155.21, 150.82, 147.26, 130.16, 129.85, 128.86,128.72, 128.13, 122.34, 121,37, 117.40, 108.89, 50.16, 27.42, 21.10; Anal. Calcd. for C24H22N202: C, 77.81; H, 5.99; N, 7.56. Found: C, 77.79; H, 6.00; N, 7.49. λ_{max} (solvent, nanometers): cyclohexane, 517; chloroform, 586.

4[2]: ^{1}H NMR (CD$_3$COCD$_3$) δ 7.75 (dd J = 14.1, 12.6 Hz, lH), 7.66 (m, 2H), 7,58 (old, J = 12.6,0.6 Hz, 1H), 7,57 (m, 3H), 7.42 (old, J = 14.2, J = 11.1 Hz, 1H), 7.11 (s, 2H), 7,09 (dd J = 13.9, 11.0 Hz, 1H), 7,01 (d, J = 14.0 Hz, lH), 3.30 (apparent t, J = 5.7 Hz, 4H), 2.72 (apparent t, J = 6,2 Hz, 4H), 1.92 (m, 4H). Anal, Calcd. for C26H24N202: C, 78.76; H, 6.10; N, 7.07. Found: C, 78.64; H, 6.16; N, 7.05. X-ray. λ_{max} (solvent, nanometers): cyclohexane, 554; chloroform, 620.

4[3]: ^{1}H NMR δ 7.79 (dd J = 14.1, 12.4 Hz, 1H), 7.59 (m, 2H), 7.52 (m, 3H), 7.32 (d, J = 12.4 Hz, lH), 7,04 (old, J = 14.3, J = 11.7 Hz, 1H), 6.94 (s, 2H), 6.84 (apparent dd J = 14.1,9.8 Hz, 1H), 6.73 (m, 2H), 6.55 (dd J = 14.0, 11.7 Hz, 1H), 3.24 (apparent t, J = 5.7 Hz, 4H), 2.73 (apparent t, J = 6.2 Hz, 4H), 1.96 (m, 4H). ^{13}C NMR δ 21.51, 27.62, 49.91, 112.12, 121.19, 122.91, 123.25, 124.98, 126.97, 128.99, 130.45, 142.20, 144.46, 147.24, 149.44, 154.14, 163.06; Anal. Calcd. for C28H26N202: C, 79.59; H, 6.20; N, 6.63. Found: C, 79.51; H, 6.15; N, 6.61.

4'[6]: ^{1}H NMR δ 7.88 (old, J 14.6, 12.2 Hz, 1H), 7.45-7.7 (m, max at 7.58, 5H), 7.37 (d, J = 12.1 Hz, 1H), 6.75-7.15 (m, d at 7.0, J = 14.6 Hz, bs at 6.88, 4H), 6.45-6.75 (m, 5H), 6.1-6.45 (m, 2H), 3.18 (t, J = 5.6 Hz, 4H), 2.74 (t, J = 6.2 Hz, 4H), 2.08 (s, 3H), 2.01, (s, 3H), 1.90-2.01 (m, max at 1,94, 4H); Anal. Calcd. for C36H36N2O2: C, 81.78; H, 6.86; N, 5.30, Found: C, 80.81; H, 6.98; N, 5.05.